

# Effects of Ga doping on the magnetic ordering of Pr in $\text{PrBa}_2\text{Cu}_3\text{O}_7$

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Neutron-diffraction and ac-susceptibility measurements have been performed to study the effects of Ga doping on the magnetic ordering of the Pr in  $\text{PrBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_7$ . The Ga atoms preferentially replace the Cu atoms in the CuO-chain layers, and this substitution is found to decrease the antiferromagnetic ordering temperature as the Ga concentration is increased. In addition, the spin arrangement along the  $c$  axis is found to change from nearest neighbors being antiparallel for  $x=0$  to nearest neighbors being parallel for  $x=0.08$  (24% Cu chain substitution); for an intermediate  $x$  of 0.04 a mixture of the two spin structures is observed. The susceptibility results exhibit Curie-Weiss behavior above  $T_N$ , and departures from this behavior in the ordered state.

Among high- $T_c$  oxides,  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  has attracted considerable attention because of its unexpected electric and magnetic properties. The introduction of Pr in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  suppresses superconductivity,<sup>1,2</sup> the Pr ions have a Neel temperature as high as 17 K, and an ordered moment as small as  $0.74\mu_B$ .<sup>3</sup> It is thus clear that interactions other than dipolar are responsible for the Pr magnetism. If superexchange is the dominant key, then those atoms located between the Pr atoms may also play important roles in Pr magnetism. An understanding of the coupling between the Pr atoms and the intermediate atoms located between them is then essential to a full understanding of the interactions involved.

There are three different types of layers of atoms that are located between the Pr atoms in  $\text{PrBa}_2\text{Cu}_3\text{O}_7$ : the CuO-chain layer, the  $\text{CuO}_2$ -plane layer, and the BaO layer. Metallic doping with Zn atoms, which substitutes for the Cu atoms located in the  $\text{CuO}_2$ -plane layers, causes the spin arrangement of Pr along the  $c$  axis to realign from antiparallel to parallel, without affecting its ordering temperature significantly.<sup>4</sup> On the other hand, a full replacement of the CuO-chain layers by TiO layers, i.e.,  $\text{PrBa}_2(\text{TiCu}_2)\text{O}_7$ , does not alter the spin structure of Pr but reduces its ordering temperature by a factor of 2.<sup>5</sup>

In this paper we report neutron-diffraction and ac-susceptibility measurements made on the  $\text{PrBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_{7-y}$  compounds to examine the effects of Ga doping on the ordering of the Pr spins. The Ga atoms replace the Cu atoms located in the CuO-chain layers. Two systems with  $x=0.04$  and 0.08 (12% and 24% replacement, respectively) were studied, and we found that both the spin structure and the ordering temperature of Pr ions are sensitive to the presence of Ga atoms. The ordering temperature decreases with increasing Ga doping, and the nearest-neighbor spins along the  $c$  axis have the tendency to realign from antiparallel to parallel.

Powder samples of  $\text{PrBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_{7-y}$  were prepared by the standard solid-state reaction technique; the details of the sample preparation techniques can be found elsewhere.<sup>6</sup> Both x-ray and high-resolution neutron diffractions were used to characterize the samples. The nominal

oxygen concentration, determined from neutron profile refinement analysis,<sup>7</sup> is 6.98(4) and 6.96(4) for the  $x=0.04$  and 0.08 compounds, respectively. Neutron-diffraction measurements were performed using the BT-9 triple-axis spectrometer at the Research Reactor at the U. S. National Institute of Standards and Technology. A pyrolytic graphite PG(002) monochromator was employed, with a PG filter placed after the monochromator position to suppress the higher-order wavelength contaminations. The energy of the incident neutrons was 14.8 meV (2.352 Å), and the angular collimations before and after the monochromator and after the sample were 40', 48', and 48' full width at half maximum (FWHM), respectively. No analyzer crystal was used in these measurements. For the low-temperature experiments, the sample was mounted in a cylindrical aluminum can filled with helium exchange gas to facilitate thermal conduction. A pumped <sup>4</sup>He cryostat was used to cool the samples, and the lowest temperature obtained was 1.36 K.

A standard subtraction technique<sup>8</sup> was used to isolate the magnetic signal from the nuclear one, where the diffraction pattern taken at a temperature well above the ordering temperature was subtracted from the one taken at low temperature. Figures 1(a) and 1(b) show the magnetic Bragg peaks observed at low temperatures for the  $x=0.04$  and 0.08 compounds, respectively. The indices shown are based on the chemical unit cell. Both the  $\{\frac{1}{2}\frac{1}{2}0\}$  type and the  $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$  type of reflections are needed in explaining the data shown in Fig. 1(a). If only one reflection is assumed for the peak that occurs at around  $2\theta=25^\circ$ , it turns out that not only the width of this peak is much too broad in comparison with the instrumental resolution but the peak position also would fit neither to the  $\{\frac{1}{2}\frac{1}{2}0\}$  reflection nor to the  $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$  reflection. In addition, the presence of the  $\{\frac{1}{2}\frac{1}{2}1\}$  and  $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$  reflections suggests the existence of the  $\{\frac{1}{2}\frac{1}{2}0\}$  and  $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$  reflections, respectively. The expected separation of the peak positions between the  $\{\frac{1}{2}\frac{1}{2}0\}$  and the  $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$  reflections is  $0.7^\circ$ , which is beyond our resolution limit. A calculation assuming the presence of both the  $\{\frac{1}{2}\frac{1}{2}0\}$  type and the  $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$  type of reflections gives excellent agreement for the peak positions and widths consistent with the instrumental resolution. The results of this calculation are

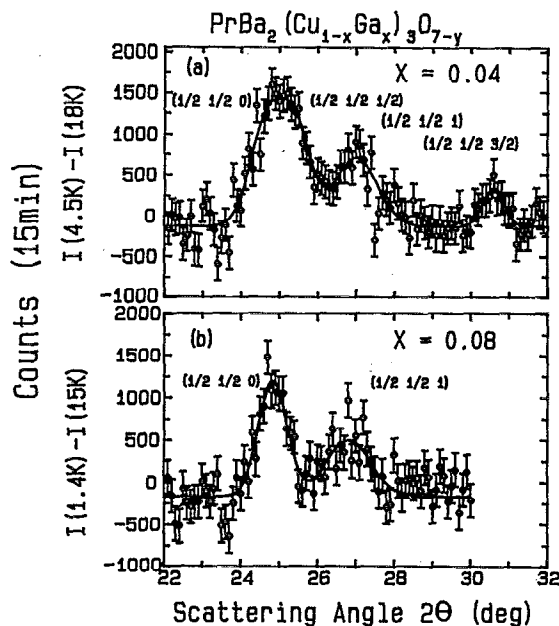


FIG. 1. Magnetic intensities in  $\text{PrBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_{7-y}$  with (a)  $x=0.04$  at  $T=4.5$  K and (b)  $x=0.08$  at  $T=1.36$  K. Both the  $\{\frac{1}{2}\frac{1}{2}0\}$  type and the  $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$  type of reflections were observed in the  $x=0.04$  compound, while only the  $\{\frac{1}{2}\frac{1}{2}0\}$  type appeared in the  $x=0.08$  compound.

shown as the solid lines in Fig. 1(a). No  $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$  type of reflections were observed in the data shown in Fig. 1(b), and the solid lines are fits based on the presence of only the  $\{\frac{1}{2}\frac{1}{2}0\}$  type of reflections.

The corresponding magnetic structure for the  $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$  wave vector is that the spins are aligned antiparallel along all three crystallographic directions, and that for the  $\{\frac{1}{2}\frac{1}{2}0\}$  wave vector is that nearest-neighbor spins along the  $c$  axis aligned parallel rather than antiparallel. Only the  $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$  type of reflections was observed in the undoped system.<sup>3,9</sup> The observations shown in Fig. 1 then indicate that introducing Ga atoms into  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  causes the Pr spins along the  $c$  axis to change from antiparallel to parallel. A 12 at. % replacement of the Cu atoms located in the CuO-chain layers by Ga atoms partially reverses the Pr spins arrangement along the  $c$  axis, and a 24 at. % replacement complete this reverse.

The temperature dependence of the  $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$  peak intensity of the  $x=0.04$  compound is shown in Fig. 2(a), while that of the  $\{\frac{1}{2}\frac{1}{2}0\}$  reflection of the  $x=0.08$  compound is shown in Fig. 2(b). Both plots reveal a typical order parameter, that measures the square of the magnetization, for powder samples. The ordering temperatures determined from the data shown in Fig. 2 give  $T_N \approx 14$  and 10 K for the  $x=0.04$  and 0.08 compounds, respectively. We note that the  $T_N$  for the undoped system is 17 K. It is then clear that the ordering temperature of Pr is quite sensitive to the presence of Ga atoms.

The ordered moment can be obtained from a comparison of the magnetic intensities to the nuclear ones, while the spin direction was determined from the relative intensities of the magnetic reflections.<sup>5</sup> The saturated moment that we obtained for the  $x=0.08$  compound using the data collected at  $T=1.36$  K is  $\langle \mu_z \rangle = 0.76 \pm 0.07 \mu_B$  with the moment directed

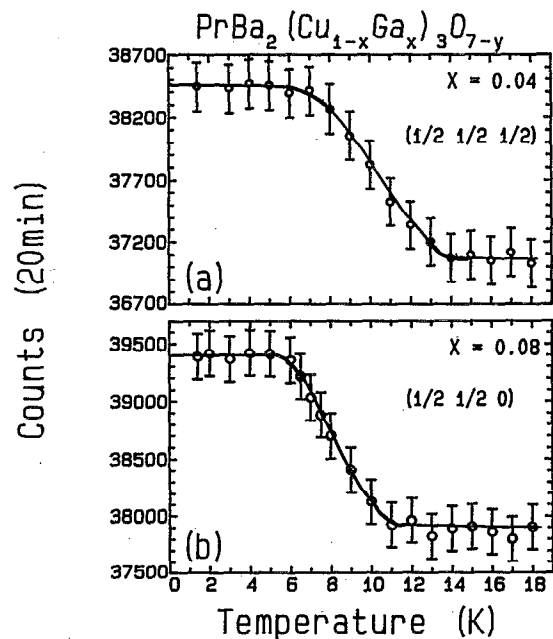


FIG. 2. Temperature dependence of the magnetic peak intensity. The Neel temperatures are determined to be 14 and 10 K for the  $x=0.04$  and 0.08 compounds, respectively. These data clearly show that the Ga doping effectively reduces the ordering temperature of the Pr spins.

along the  $c$  axis. This value of the ordered moment and the spin direction are the same as that found in the undoped system. Thus the Ga atoms do not alter the spin direction or the size of the ordered moment. Based on these results, the percentage in which the spin arrangement along the  $c$  axis has been reversed can be estimated by comparing the observed intensities between the  $\{\frac{1}{2}\frac{1}{2}0\}$  type and the  $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$  type of reflections. A calculation using the  $\{\frac{1}{2}\frac{1}{2}0\}$  and  $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$  intensities observed in the  $x=0.04$  compound indicates that 80% of the sample has its Pr spins aligned parallel along the  $c$  axis. A calculation using the  $\{\frac{1}{2}\frac{1}{2}1\}$  and  $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$  reflections gives the same value.

The ac susceptibility was measured using the Lake Shore 7221 ac susceptometer. Portions of the real part of the measured ac susceptibility for both compounds are shown in Fig. 3. These data were taken with an alternating magnetic field of strength 3 Oe and frequency 300 Hz; data collected with a frequency as high as  $10^4$  Hz generated the same results. Above the Neel temperature of Pr, the data follow a Curie-Weiss law very well all the way up to the highest temperature studied of  $T=320$  K. However, a small temperature-independent term  $\chi_0$  is also needed in describing the data. The solid lines shown in Fig. 3 are obtained by fitting the data to  $\chi_0 + C/(T + \theta)$  for  $30 \text{ K} < T < 320 \text{ K}$ . The effects of the Pr ordering on the ac susceptibility are clearly seen. At low temperatures the data deviate from the fitted Curie-Weiss curves, and the temperatures at which these deviations begin agree very well with the  $T_N$  of Pr observed using neutron diffraction. However, no cusp on the  $\chi_{ac}-T$  curve, typical of antiferromagnetic ordering, is observed.

The effective moment  $\mu_{\text{eff}}$  that we obtained using the fitted values for the Curie-Weiss constants  $C$  are 3.39 and

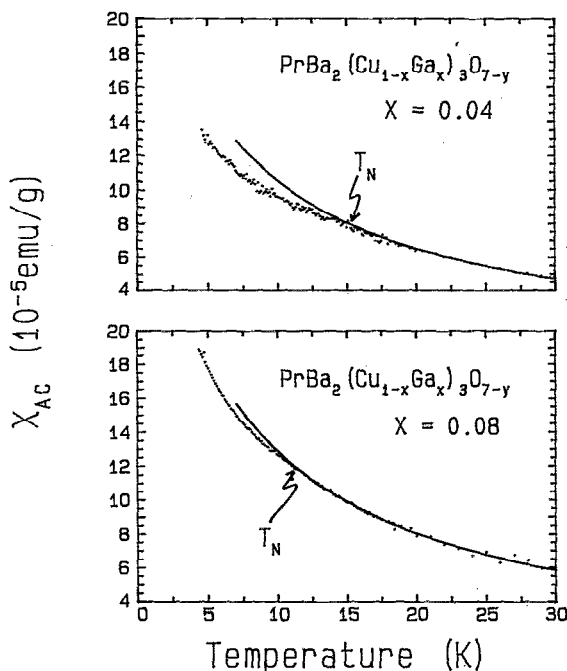


FIG. 3. Portions of the measured ac susceptibility as a function of temperature. The solid lines shown are fitted Curie-Weiss curves using data collected in the temperature range of  $30\text{ K} < T < 320\text{ K}$ . Departures from the fitted curves at low temperatures are clearly seen. The temperatures at which the departures begin match very well to the Neel temperature determined using neutron diffraction.

$3.01\mu_B$  for the  $x=0.04$  and  $0.08$  compounds, respectively. These values are smaller than the value of  $3.58\mu_B$  expected for free ions. We believe that the reduction of the effective moment is likely due to the crystalline electric field effects.

As the Ga doping is increased the effect becomes more pronounced and hence the effective moment is much reduced.

In conclusion, the ordering temperature of the Pr spins is effectively reduced by Ga doping, while it is not affected by Zn doping.<sup>4</sup> The Ga atoms substitute into the CuO-chain layers, and the Zn atoms into the CuO<sub>2</sub>-plane layers. It is then clear that the CuO-chain layers are more responsible than the CuO<sub>2</sub>-plane layers for the high ordering temperature of Pr observed in PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>.

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